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Co-Pyrolysis of Waste Polystyrene Foam and Microalgae at Low Temperatures †

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Abstract: Fossil fuel reserves have depleted. So, renewable and sustainable energy form an important issue. Microalgae as a third generation biomass can be an alternative carbon neutral fuel source. But its fuel quality is low. Co-pyrolysis is important technique to upgrade fuel quality of microalgae. In this study, we aimed to carry out pyrolysis of polystyrene and *Spirulina* sp. microalgae at low temperatures (350, 400, 450 °C). The experiments were done by using semi-batch reactor setup. Co-pyrolytic product yields were calculated. Composition of liquid products was enlightened by using GC-MS. As a result of the analysis, it was detected aromatic compounds like styrene, toluene in the co-pyrolytic liquid. Besides that it was observed co-pyrolysis was increased solid residue yield while it was decreased liquid and gas product yield.

Keywords: polystyrene; plastic wastes; microalgae; biomass; pyrolysis

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1. Introduction

Global warming causes the environmental changes. It has been known that the reason of global warming is human activities. Humans effect on global warming by using fossil fuel in a huge amount [1]. While anthropogenic activities cause fossil fuel depletion, the wasted materials which are called as municipal solid waste (MSW) can be used as energy feedstock. These energy sources can be transformed to fuel via thermochemical conversion technologies such as pyrolysis, gasification, carbonization, incineration. It can be possible to meet electricity needs via these technologies too [2].

Pyrolysis process is carried out at 300–1200 °C in the absence of oxygen. With its this aspect, pyrolysis differs from combustion. Nowadays, pyrolysis has been used to produce catalysis, hydrogen and chemicals [2]. Besides that, pyrolysis has more advantages than other thermochemical routes. Firstly, low energy consumption occurs in pyrolysis process compared to gasification. Secondly, harmful gases are produced in relatively low amount. Lastly, the process can be formed and moved to another place easily [3].

Based on the data which was obtained at 2020, nearly 3 million tons of plastic packaging materials are collected in the landfills in Europe [4]. There are so many researches in scientific literature about plastic waste such as Polystyrene (PS) [5], Polypropylene (PP) [6], Low Density Polyethylene (PE) [7] pyrolysis.

Carbon neutral fuels have huge importance on the sustanability. Microalgae as an non-edible feedstock occur an alternative to the first generation biomass sources [8]. However, it has been known that the fuel which is obtained from microalgae pyrolysis has some disadvantages like high humidity and protein content. So co-pyrolysis with several materials like tires, plastics and bamboo waste seems the good way to obtain high quality fuel [9]. In this study, it was aimed to determine the effect of blending PS to SP feed on the liquid yield and composition compared to PS pyrolysis. The experiments were conducted several temperatures which were selected as possible as low.

2. Material and Methods

The plastic waste source, polystyrene (PS) foam, was supplied as an electronic device package. Before the pyrolysis it was divided small pieces in rectangular prism shape and dried in oven. The aim of this drying was to fit PS in the glass reactor. Because expanded PS was used and it was known that over 90 percentage by volume of expanded included air [10]. The microalgae source, *Spirulina* (SP), was bought in powder form commercially. The properties of SP were shown in Table 1. The amount of the oxygen in SP was decided by the difference. Pyrolysis setup covers ceramic furnace, Nitrogen bottle, PID temperature controller, thermocouples, glass reactor and condensers. The setup was shown in Figure 1. For experiments, firstly the feedstock was weighted. And then, the feedstock was put in the glass reactor whose weight was known. Then, the reactor was settled in the vertical furnace. The glass equipments were combined each other. Circulator was arranged at 0 °C and worked. The temperature in the reactor was shown by using digital thermocouple. The temperature in the furnace was arranged by utilizing PID controller. Before the experiments, setup was purged with nitrogen. Then, the experiment was carried out at the desired temperature. After the experiment, product yields were calculated with respect to the amount of the occurring products. Liquid products were analysed via GC-MS. Co-pyrolysis of SP and PS was done by adding equal amount of feedstock to the reactor. For comparing the results, pristine PS pyrolysis was done at the same temperatures. Effect of temperature (350, 400, 450 °C) on the liquid yield and composition was investigated. Besides that, other product yields (solid, gas) and total conversion (gas + liquid) values were computed.

Figure 1. Pyrolysis setup [11].

Table 1. Elemental composition of SP feedstock (ash free and dry basis) [12].

Elements	Amount (%, wt./wt.)
C	46.69
H	6.22
N	10.76
S	1.55
O	34.78

3. Results and Discussion

As shown in Figure 2, compared to individual pyrolysis of PS, co-pyrolysis was decreased the liquid yield at all temperatures. For co-pyrolysis of SP and PS, maximum liquid yield was observed at 450 °C. It was determined that SP and PS co-pyrolytic liquid included mainly styrene and styrene derivative methyl styrene. It was estimated that observed phenol in the co-pyrolytic liquid originated from SP's thermal degradation [8]. In Figure 3, it was shown the chromatogram of co-pyrolytic liquid and virgin polystyrene.

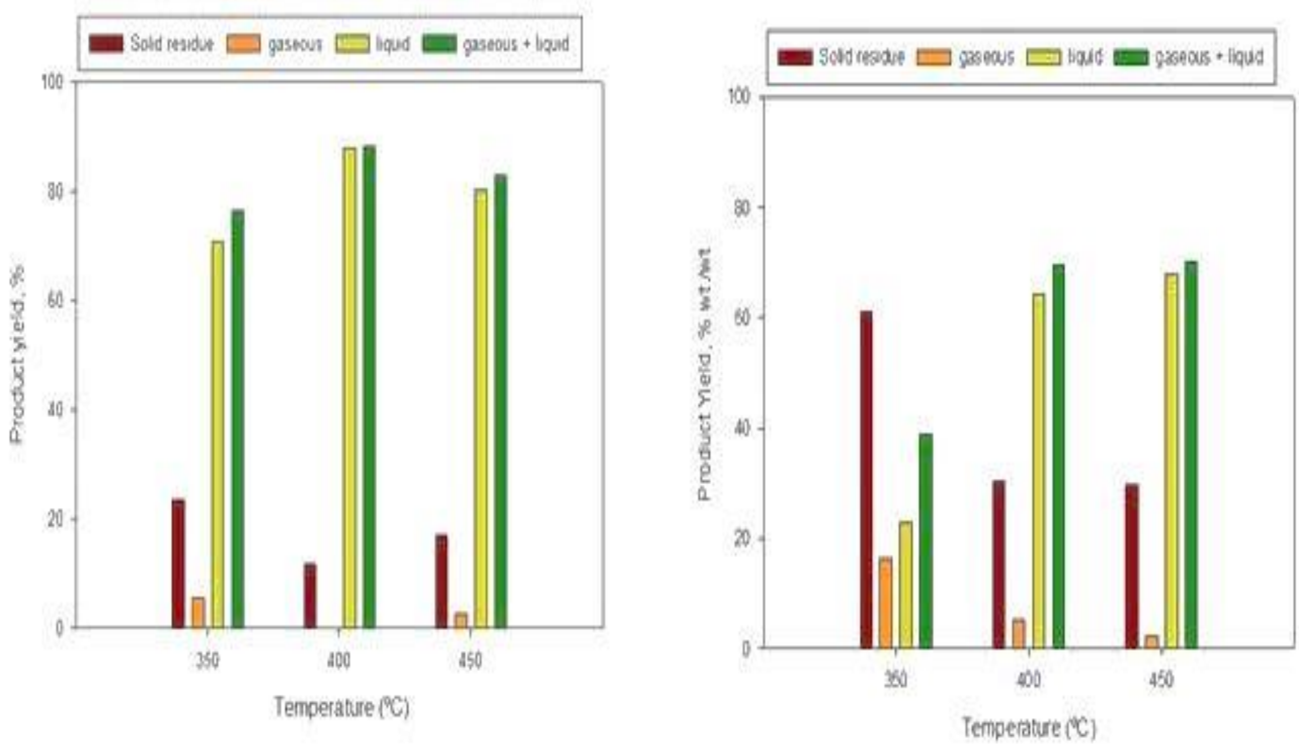

Figure 2. Pyrolytic product distribution by weight for PS (**left**) and PS:Algae (1:1) (**right**).

In Table 2, it was shown the component distribution of polystyrene as a result of the thermal cracking. So, the liquid composed of mainly aromatic hydrocarbons. It was observed that the styrene and its derivative alpha-methyl styrene effected temperature significantly. And as expected, styrene was the main component.

Table 2. Detecting main components in the pyrolytic liquid of PS by GC-MS.

Compound	Peak Area (%)		
	350 °C	**400 °C**	**450 °C**
benzene	0.5	0.85	0
toluene	9.25	3.5	6.6
ethyl benzene	8.75	4.7	7.92
styrene	46.7	16.05	29
methyl styrene	24.15	9.5	10.6

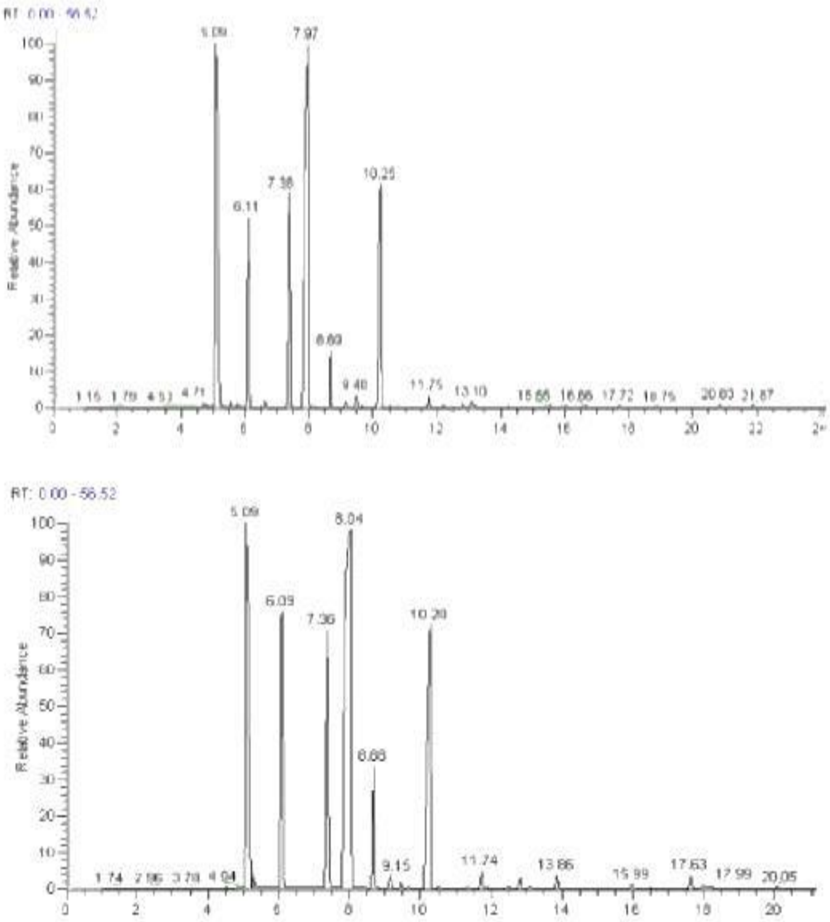

Figure 3. GC-MS chromatogram for the Liquid Product obtained from PS-Algae co-pyrolysis (**up**) and PS pyrolysis (**down**) at 450 °C.

In Table 3, detected compounds in co-pyrolytic liquid of SP and PS were shown. Phenol which was not observed in the PS liquid was obtained in the bio-oil. Interestingly, at 400 °C, styrene and alpha-methyl styrene amount were found as higher than pristine PS liquid. This can be originated from synergistic effects between PS and SP.

Table 3. Detecting main components in the pyrolytic liquid of PS-Algae by GC-MS.

Compound	**Peak Area (%)**		
	350 °C	**400 °C**	**450 °C**
toluene	5.5	6.62	5.9
ethyl benzene	7.25	9.66	7.85
styrene	24.8	26.89	26.7
phenol	0	1.2	0.9
methyl styrene	9.45	14	10.65

4. Conclusions

Co-pyrolysis of PS and SP was conducted at 350–450 °C. At this temperature range, the liquid product compositions were determined by using GC-MS. As a result of the co-pyrolysis, it was observed oxygenated compound, phenol. Synergistic effects between the feedstocks enabled to increase toluene, ethyl benzene, styrene, alpha-methyl styrene amount at 400 °C.

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